A chiroptical molecular switch with distinct chiral and photochromic entities and its application in optical switching of a cholesteric liquid crystal

van Delden, R.A.; Mecca, T.; Rosini, C.; Feringa, B.L.

Published in:
Chemistry : a European Journal

DOI:
10.1002/chem.200305276

A Chiroptical Molecular Switch with Distinct Chiral and Photochromic Entities and Its Application in Optical Switching of a Cholesteric Liquid Crystal

Richard A. van Delden,[a] Tommaso Mecca,[b, c] Carlo Rosini,*[b] and Ben L. Feringa*[a]

Abstract: Two new structurally related photoswitches are described, in which azobenzene photochromism is combined with the chirality of a 2,2′-dihydroxy-1,1′-binaphthyl unit. In system **1** the chiral binaphthyl moiety is bridged by a methylene tether, locking the biaryl chirality while in system **2** the biaryl core is unbridged and has considerable conformational flexibility. Both compound are capable of inducing cholesteric liquid crystalline phases and proved to be good photoswitches both in solution and in a liquid crystalline matrix. Compound **2** is capable of completely reversing the liquid crystalline chirality which is unique for a chiroptical molecular switch where the switching unit and the chiral moiety are separate entities.

Keywords: biaryls · chirality · isomerization · liquid crystals · molecular switches · photochromism

Introduction

Molecular switches are prominent members of the toolbox of nanotechnology.[1] The broad current interest in bistable molecular systems, which can function as molecular switches, has resulted in a large variety of organic structures which potentially can be applied for example in optical data storage and processing.[2] The most widely studied class of molecular switches are based on photochromic molecules where light can be used as a stimulus for switching.[3] Requirements for applications of these systems, such as high switching selectivity and fatigue resistance, have been met by fine-tuning of the different molecular structures.[2] A number of switching systems was also shown to function in processable media, which is absolutely essential for any nanotechnological application. Typical materials include photochromic (doped) polymers[4] or polypeptides,[5] crystals,[6] and liquid crystals.[7] Usually photochromism is monitored by UV/Vis spectroscopy at the absorption maxima of the bistable molecular system but in an application as light-controlled molecular switches this implies destructive read-out. In order to meet the requirement of non-destructive read-out chiroptical molecular switches based on the photochromism of chiral sterically overcrowded alkenes have been developed.[8] These overcrowded alkenes are unique because switching results in a reversal of the intrinsic chirality, changing the handedness of the helicity of the system. Two types of switches based on sterically overcrowded alkenes were developed (Figure 1): A) enantiomeric photobistable molecules where two enantiomers are interconverted at a single wavelength by changing the handedness of the circularly polarized light, and B) diastereomeric photobistable molecules where the photochromic compound consists of two pseudoenantiomeric forms of opposite helicity which

[a] Dr. R. A. v. Delden, Prof. Dr. B. L. Feringa
Department of Organic Chemistry
Stratingh Institute, University of Groningen
Nijenborgh 4
9747 AG Groningen (The Netherlands)
E-mail: feringa@chem.rug.nl

[b] Dr. T. Mecca, Prof. Dr. C. Rosini
Dipartimento di Chimica
Università della Basilicata
Via N. Sauro 85
85100 Potenza (Italy)
E-mail: rosini@unibas.it

[c] Dr. T. Mecca
Current address:
C.N.R.—Istituto di Chimica Biomolecolare (Sez. di Catania)
Via del Santuario 110
95028 Valverde, Catania (Italy)

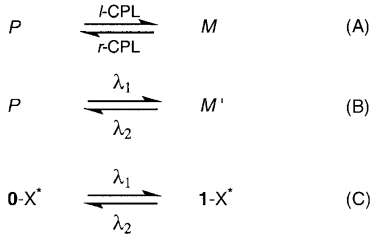
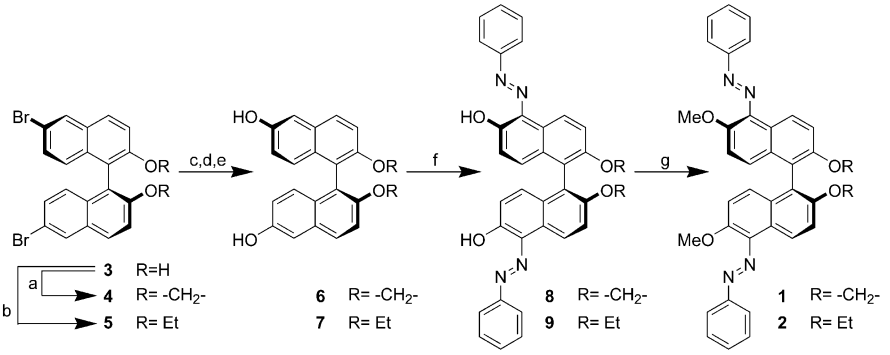


Figure 1. Schematic representation of different types of chiroptical molecular switches (X* = chiral auxiliary group).

 DOI: 10.1002/chem.200305276

can undergo photoisomerization by irradiation at two different wavelengths λ_1 and λ_2.

Both systems can be read-out in a non-destructive manner by optical rotation employing wavelengths far outside the absorption bands of either of the bistable molecular forms of the switchable system. The photomodulation of intrinsic chirality also offers the possibility of using these systems as triggers of liquid crystalline phase transitions where the chirality of a chiral nematic (cholesteric) liquid crystal is fully controlled by using a chiroptical molecular switch as a dopant.[9] Steric hindrance resulting in an intrinsic helical structure is an essential feature in all the switchable chiral alkenes developed so far. There are a number of other examples of chiral optical switches but in most of these systems the photochromic part and the chiral part are separate entities. In these cases switching does not change the chirality of the system although it can have a substantial influence on the chiral properties (Figure 1C).[2,10] Some of these systems, which are based on different types of photochromism, have been employed in liquid crystals and could influence the chiral properties of the systems but not control the handedness of the cholesteric phase, that is, the magnitude but not the sign of the cholesteric pitch could be switched by light in a reversible manner.[11] Very recently, for example, an axially chiral photoswitchable compound based on azobenzene photochromism combined with binaphthalene chirality was reported.[12] With this system doped in nematic liquid crystalline hosts, it was possible to induce cholesteric phases by the influence of the chiral binaphthyl part of the dopant and to influence the chiral properties by photoinduced *trans–cis* isomerization of the photochromic azobenzene part of the dopant. The handedness of the liquid crystalline phase, however, remained the same. Here we report on two structurally related systems, in which azobenzene photochromism is combined with the chirality of 2,2′-dihydroxy-1,1′-binaphthyl (BINOL), a source of chirality which is nowadays easily available and has found a myriad of applications as chiral ligand and catalyst in asymmetric synthesis.[13] The new photochromic compounds (*S*)-**1** and (*S*)-**2** are shown in Scheme 1. These two compound were designed as phototriggers for liquid crystalline phase transitions. Functionalized 1,1′-binaphthalenes are very efficient dopants to induce chiral nematic LC phases and high helical twisting powers are observed due to the intrinsic chirality of the binaphthalene core (see below).[14] It was established that the chiral induction is highly dependent on the dihedral angle (θ) between the two naphthalene moieties.[15] In the most commonly observed *cisoid* conformation ($\theta < 90°$), an (*S*)-binaphthalene compound induces a positive cholesteric phase while in the *transoid* ($\theta > 90°$) conformation a negative cholesteric phase is induced by an (*S*)-binaphthalene compound.



Scheme 1. Synthesis of enantiomerically pure chiroptical molecular switches (*S*)-**1** and (*S*)-**2** starting from (*S*)-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthalene **3**: a) K_2CO_3, DMF, CH_2I_2, 80°C, 78%;[17] b) K_2CO_3, DMF, CH_3CH_2Br, 80°C, 88%; c) *n*BuLi, −78°C; d) $BF(OCH_3)_2$, −78°C; e) $NaOH/H_2O_2$, 0–20°C (yields (*S*)-**6**: 86%, (*S*)-**7**: 72%); f) benzenediazonium tetrafluoroborate salt, pyridine and K_2CO_3 in anhydrous THF, −20°C (yields (*S*)-**8**: 38%, (*S*)-**9**: 43%), g) MeI/K_2CO_3 in DMF (yields (*S*)-**1**: 65%), (*S*)-**2**: 66% yield).

For compounds **1** and **2**, the intrinsic chirality of the binaphthyl-based core should guarantee the induction (in a nematic solvent) of cholesteric mesophases. The azobenzene moieties are oriented in the same direction as the axis joining the two naphthalene moieties. In LC hosts, binaphthalenes are known to orient with this axis parallel to the nematic director.[14a] In compound **1** the chiral binaphthalene core is rigidified by a methylene bridge in order to minimize the influence of azobenzene photoisomerization on rotation around the biaryl bond as the compound is fixed in a *cisoid* conformation (note that racemization cannot occur under the present conditions). In compound **2** the chiral binaphthalene core has more rotational freedom and the influence of photoisomerization of the azobenzene on the overall geometry of the molecule could be more pronounced. We anticipated a major influence of azobenzene switching on the overall conformation, and as a consequence the chirality, of the compounds which could lead to chiroptical switching of the handedness of these cholesteric phases.

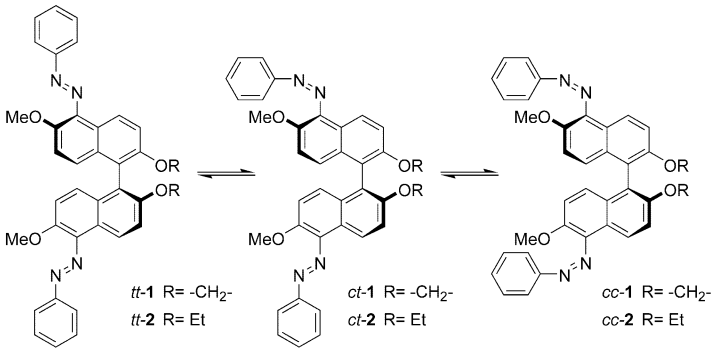
The photochromic and chiral properties of these two systems were studied both in solution and in liquid crystalline (LC) environment.

Results and Discussion

Synthesis: Compounds (*S*)-**1** and (*S*)-**2** were synthesized starting from (*S*)-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthalene[16] in four steps: 1) protection of the hydroxy groups in 1,1′-position of the binaphthalene rings;[17] 2) substitution of the two bromine atoms in 6,6′-position with two hydroxy groups; 3) coupling reaction with the benzenediazonium tetrafluoborate salt and 4) methylation of the two hydroxy groups in 6,6′-position of the binaphthalene moiety (Scheme 1).

The presence of two azobenzene moieties in both compound **1** and **2** allows the existence of three isomers, the energetically preferred all-*trans* C_2-symmetric isomer (*tt*), the

mixed *cis–trans* isomer (*ct*) and the all-*cis* C_2-symmetric isomer (*cc*). These forms can be interconverted by photoinduced isomerization of the photochromic azobenzene moieties (Scheme 2). A substantially steric influence of the binaphthalene core on the overall geometry and chirality



Scheme 2. Possible photochemical interconversions between three compounds differing in azobenzene geometry.

upon photoisomerization is expected. Whereas in the all-*trans* configuration of **1** and **2** the linear orientation around the azo double bond allows for the phenyl group to simply bend away, upon *trans* to *cis* isomerization steric interactions are severely increased and the chiral binaphthyl unit is expected to exert an effect on the orientation of the azophenyl moiety. Pure—energetically favorable—*tt*-(*S*)-**1** and *tt*-(*S*)-**2** were obtained by heating any mixture of *tt*, *ct* and *cc* isomers to allow thermal equilibration. The UV/Vis and CD spectra of both *tt*-(*S*)-**1** and *tt*-(*S*)-**2** are depicted in Figure 2.

Upon comparison of compound **1** and **2** distinct differences in the UV/Vis absorption are observed. First of all, it is interesting to compare the absorption spectra of (*S*)-**1** and (*S*)-**2** with the corresponding spectra of (*S*)-2,2′-methylenedioxy-1,1′-binaphthyl (*S*)-**10** and (*S*)-2,2′-dimethoxy-1,1′-binaphthyl (*S*)-**11**, that is, the compounds which are the model compounds of the core of (*S*)-**1** and (*S*)-**2** (Figure 3).[18]

In the spectra of those model compounds, two main region of absorption, can be easily singled out: a) 350–250 nm and b) 250–200 nm. As it is well known, region a is due to the ^{1}La transition (short axis polarization) while region b) is due to the ^{1}B transition (long axis polarization) of the naphthalene chromophore.[18] Interestingly, the absorption of these model compounds is almost negligible at 250 nm and the extinction coefficient at about 300 nm is in the range of 7000–8000, therefore the strong absorption bands (ε 20000 or even more), present in the spectra of both (*S*)-**1** and (*S*)-**2** at wavelengths longer than 300 nm, are related to the aromatic azo-moieties. As a matter of fact, *trans*-phenyl-N=N-(1-naphthyl) shows absorptions at 454 nm (ε_{max} 450, n→π* transition) and 371 nm (ε_{max} 22900, π→π* transition),[19] therefore we can conclude that the bands observed for (*S*)-**1** and (*S*)-**2** at about 460 and 400 nm are due to the n→π* and π→π* transitions of the aromatic azochromophore, respectively. The wavelength shift is due the presence of the substituents in both (*S*)-**1** and (*S*)-**2**. By contrast, the intense bands at λ <250 nm are certainly due to the binaphthyl chromophore, in particular the sequence of a

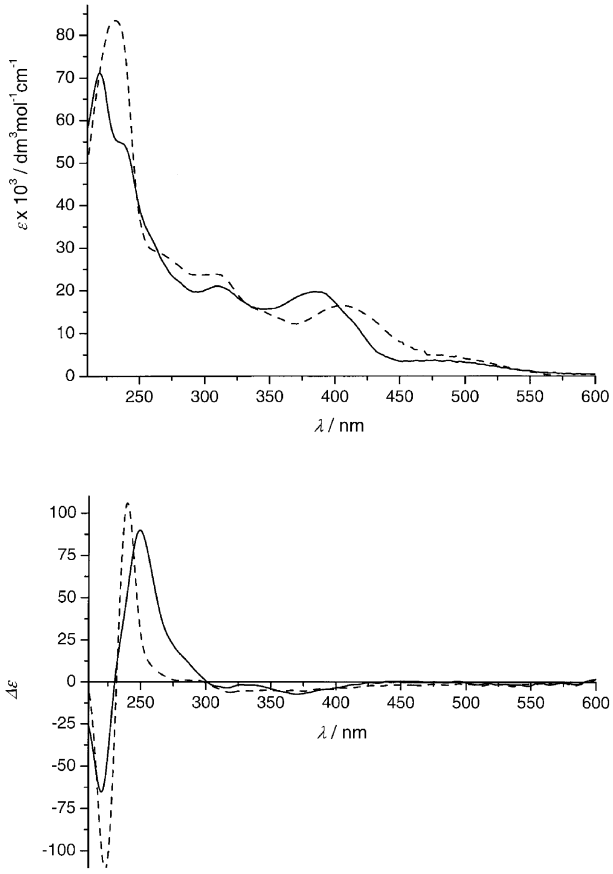


Figure 2. UV/Vis and CD spectra of (*S*)-*tt*-**1** (——) and (*S*)-*tt*-**2** (-----) in *n*-heptane solution.

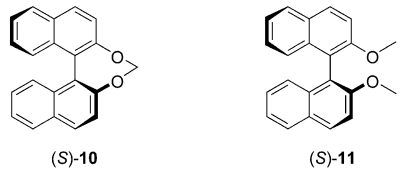


Figure 3. Model compounds (*S*)-**10** and (*S*)-**11**.

shoulder at about 230 nm followed by a maximum at about 220 nm is clearly indicative of the presence of a small dihedral angle between the naphthyl rings (in fact (*S*)-**1** is a bridged binaphthyl compound) whilst the broad peak at 230 nm for (*S*)-**2** clearly reveals a larger dihedral angle between the aromatic rings,[18] as it is certainly true for the open derivative (*S*)-**2**. In the CD spectra, the excitations of the azo-moieties (wavelengths longer than 300 nm) give rise to only relatively weak Cotton effects, whilst a strong, positive couplet in the spectra of (*S*)-**1** and (*S*)-**2** shows clearly the existence of *cisoid* binaphthyl chromophores, taking into account that both these compounds have (*S*) absolute configuration.[18] The absorption band at 390 nm of *tt*-(S)-**1** is bathochromically shifted to 405 nm for *tt*-(*S*)-**2**. Similarly, the absorption band at 450 nm of *cc*-(*S*)-**1** is red-shifted to 460 nm for *cc*-(S)-**2**. This effect can be ascribed to an in-

creased contribution of the lone pairs of the oxygens in 1,1′-position of the binaphthyl group to the delocalized π electronic system.[20] This should have a small but distinct effect on the photochemical properties.

Isomerization in solution: Solutions of pure *tt*-(*S*)-**1** in chloroform and *n*-heptane (10^{-5} M) were irradiated at different wavelength (391, 396, 450 nm) and the change in UV/Vis absorption and circular dichroism (CD) was monitored. From the ratio of the different absorption curves, the most ideal wavelength for *trans* to *cis* and the reverse *cis* to *trans* isomerization were determined to be 396 and 450 nm, respectively. The UV/Vis and CD characteristics of compound (*S*)-**1** in chloroform and *n*-heptane are similar. The UV/Vis and CD spectra corresponding to the two photostationary states at 396 and 450 nm in *n*-heptane solution are depicted in Figure 4, together with the UV/Vis absorption of the initial *tt*-(*S*)-**1** solution.

The photostationary state ratios of the three forms (Table 1) were analyzed by HPLC and the three geometrical isomers could be assigned by diode-array UV/Vis analysis. Only starting from chloroform solution full baseline separation of the three isomers was achieved and the ratios in this solvent are reported. Analysis of the not fully separated

Table 1. Ratios of the three geometrical isomers of (*S*)-**1** at the photostationary states in chloroform.[a]

λ [nm^{-1}]	*tt*-(*S*)-**1** [%]	*ct*-(*S*)-**1** [%]	*cc*-(*S*)-**1** [%]
396	19	46	35
450	67	30	3

[a] As determined by HPLC analysis on silica gel using $CHCl_3/Et_2O$ 98:2 at 0.25 mL min^{-1} and 296 nm (which is an isosbestic point of the three form this eluent) as a detection wavelength. The elution order is: *tt*-(*S*)-**1** (16.5 min), *ct*-(*S*)-**1** (23.0 min) and *cc*-(*S*)-**1** (28.5 min).

HPLC traces and UV/Vis and CD spectra from *n*-heptane solution revealed similar switching selectivities in this solvent. The first (least polar) eluted fraction shows a UV/Vis spectrum coincident with the spectrum of the initial compound after the thermal isomerization, and it was assigned the *trans–trans* (*tt*) structure. The third (most polar) fraction shows a UV/Vis spectrum characterized by the disappearance of the absorption bands at $\lambda = 390$ nm and $\lambda = 480$ nm and the appearance of a broad band at $\lambda = 450$ nm that is typical of a *cis*-azobenzene moiety.[21] It was assigned the *cis–cis* (*cc*) structure. The second substance eluted (intermediate polarity) shows an UV/Vis spectrum that is exactly the average of the spectra of the two previous compounds, so it is safe to assign to this compound the *cis–trans* (*ct*) structure.

After 396 nm irradition 58% of all azobenzene units are switched to the *cis* configuration, subsequent irradiation at 450 nm results in a photostationary state in which 82% of all azobenzene units are present in *trans* form. The presence of an isosbestic point at 269 nm indicates a clean switching process which was shown to be fully reversible. From the photostationary state ratios and UV/Vis spectra, the absorption spectra of *ct*-**1** and *cc*-**1** could be calculated (Figure 5). These spectra and also analysis of the UV/Vis spectra obtained directly from the HPLC detector show that the absorption spectrum of *ct*-(*S*)-**1** is the exact average of the spectra of the all-*trans* and all-*cis* forms of (*S*)-**1**. In this C_2-symmetrical system, the two azobenzene units act as separate entities. The ratios observed for both photostationary

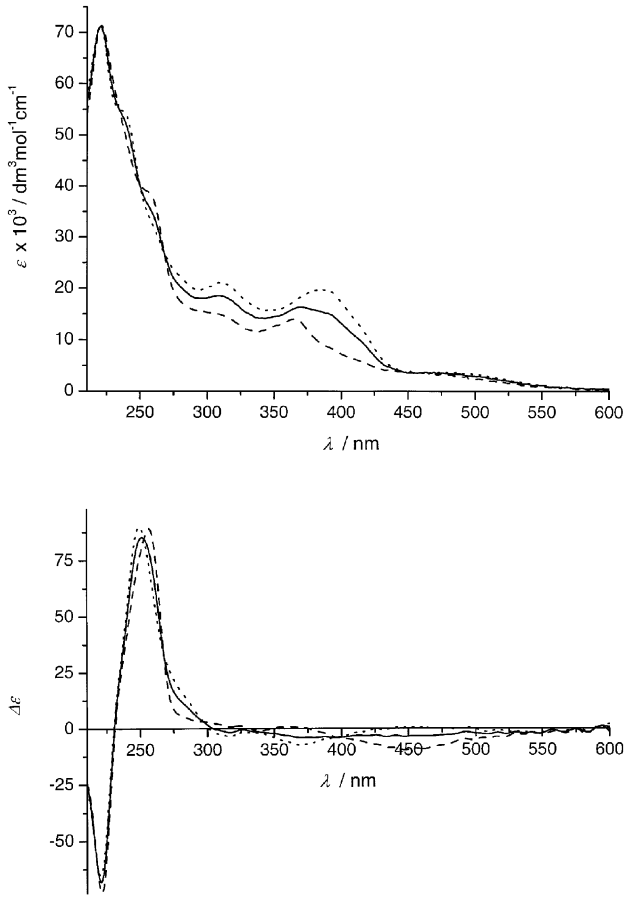


Figure 4. UV/Vis and CD spectra of (*S*)-**1** in *n*-heptane solution: ——, photostationary state at 450 nm (excess *trans*); -----, photostationary states at 396 nm (excess *cis*). The original spectra of pure *tt*-(*S*)-**1** are plotted for comparison (•••••).

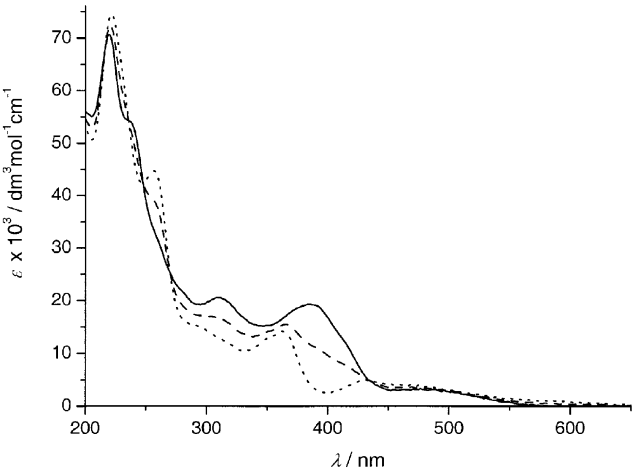


Figure 5. Calculated UV/Vis spectra of the three isomers *tt* (——), *ct* (-----) and *cc* (*S*)-**1** (•••••) in *n*-heptane.

states are a near statistical distribution of the amount of *trans* and *cis* azobenzene units. The most apparent feature of these spectra is that the difference between the UV/Vis spectra of the all-*trans* compound *tt*-(*S*)-**1** and both *cis*-compounds *ct*-(*S*)-**1** and *cc*-(*S*)-**1** is relatively small compared to other azobenzene photochromic compounds reported.[22] This small difference results in a relatively modest switching efficiency but nevertheless it is shown here that compound (*S*)-**1** can readily function as a molecular switch in chloroform and *n*-heptane solution. From the CD spectra of both photostationary states and the initial *tt*-(*S*)-**1** isomer (Figure 4) only a minor influence of azobenzene isomerization on the overall geometry and chirality of this compound is observed. This was expected since the intrinsic chirality of the binaphthalene core is fixed by the methylene tether.

Compound (*S*)-**2** was analyzed in the same manner using a 10^{-5} M solution of pure *tt*-(*S*)-**2** in chloroform and *n*-heptane. As for compound **1**, UV/Vis and CD spectra as well as switching selectivities were comparable in both solvents. The most efficient wavelengths for the switching process were determined to be 405 nm for the *trans* to *cis* isomerization and 466 nm for the reverse process. The photoisomerization showed a clear isosbestic point at 271 nm (Figure 6). The photostationary state ratios are shown in Table 2.

Comparable to compound **1**, the HPLC analysis of the photostationary states show the presence of three isomers

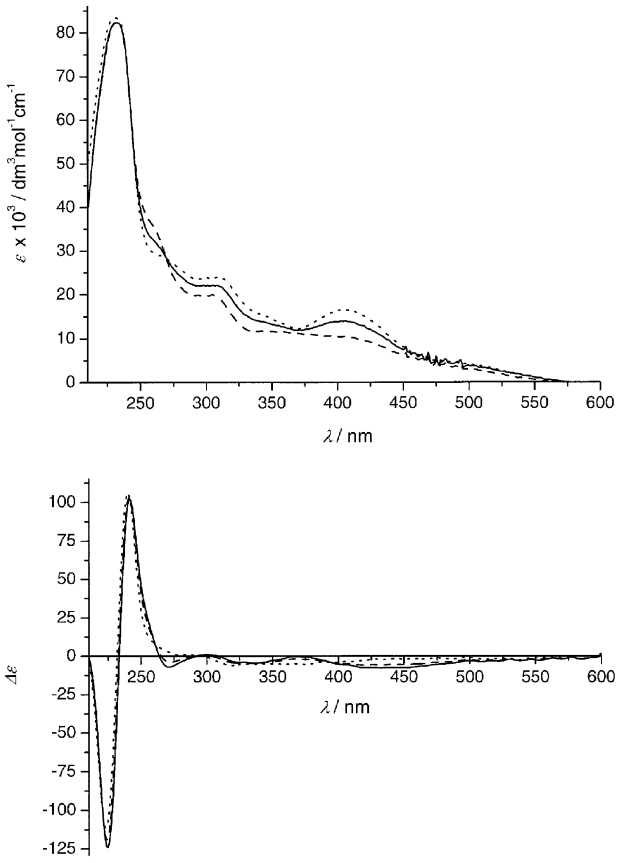


Figure 6. UV/Vis and CD spectra of (*S*)-**2** in *n*-heptane solution: ——, photostationary state at 466 nm (excess *trans*), -----, photostationary states at 405 nm (excess *cis*). The original spectra of pure *tt*-(*S*)-**2** are plotted for comparison (•••••).

Table 2. Photostationary state ratios of the three isomers of (*S*)-**2** in chloroform.[a]

λ [nm^{-1}]	*tt*-(*S*)-**2** [%]	*ct*-(*S*)-**2** [%]	*cc*-(*S*)-**2** [%]
405	33	46	21
466	56	40	4

[a] As determined by HPLC analysis on silica using $CHCl_3/Et_2O$ 98:2 (0.25 mL min^{-1}) and HPLC analysis using the same conditions as for **1** using a detection wavelength of 245 nm (isosbestic point of the three forms in this eluent). The elution order is the same as for compound **1**: *tt*-(*S*)-**2** (13.8 min), *ct*-(*S*)-**2** (18.3 min) and *cc*-(*S*)-**2** (21.4 min).

easily assignable to the *tt*, *ct* and *cc* (*S*)-**2**. Also for this compound the absorption spectrum of *ct*-(*S*)-**2** is the exact average of the spectra of the all-*trans* and all-*cis* forms of (*S*)-**2**, and the absorption difference between the *cis*- and *trans*-forms are less pronounced than expected. The calculated spectra for *ct*-**2** and *cc*-**2** are depicted in Figure 7.

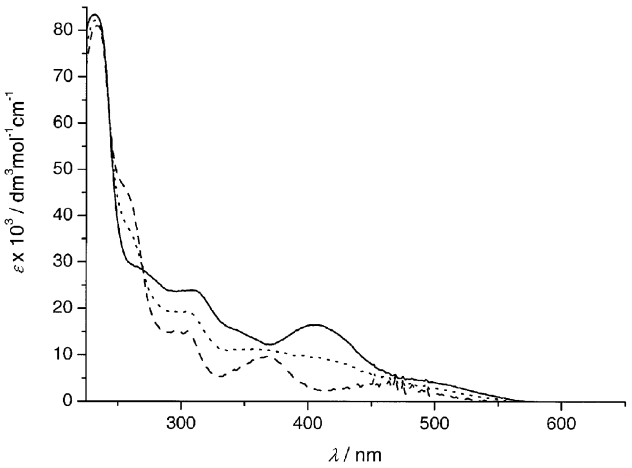


Figure 7. Calculated UV/Vis spectra of the three isomers *tt* (——), *ct* (-----) and *cc* (*S*)-**2** (•••••) in *n*-heptane.

When the wavelength of 405 nm is used to promote the *trans*- to *cis*-isomerization process, only 44 % of all *trans*-azobenzene moieties present are switched to the *cis*-form. Subsequent irradiation at 466 nm results in a photostationary state in which 76 % of the azobenzenes units are present in the *trans*-form. Also, the observed ratios reflect a near statistical distribution of *trans*- and *cis*-azobenzene units and no combined effect of the two units present in each molecule is observed.

Also for compound **2** the effect of *cis–trans* isomerization on the chirality of the compound was studied by circular dichroism (Figure 6). The most striking observation here is that the effect of this isomerization is similar to the effect observed for (*S*)-**1**. Although some changes in CD can be observed upon irradiation the overall chirality of the system is more or less retained even though the rotational freedom of the binaphthalene core is far larger than for compound (*S*)-**1**. The bisignate CD band around 240 nm reflecting the chirality of the binaphthalene core is hardly changed upon photoirradiation. The relative changes in the bathochromic side of the spectrum are more pronounced, comparable to

the changes observed for compound (*S*)-**1**. Compound (*S*)-**2** was shown to be a—though moderate—molecular switch in these solution experiments. Both compounds were subsequently examined in liquid crystalline hosts.

Photomodulation of cholesteric liquid-crystalline mesophases: The behavior of (*S*)-**1** and (*S*)-**2** was studied in E7 (a commercially available nematic mixture of different biphenylcarbonitrile-based mesogens, liquid crystalline up to 58 °C). All samples were prepared with a concentration of active compound (*tt*-(*S*)-**1** or *tt*-(*S*)-**2**) of three weight %. The pitches of the induced cholesteric mesophases were determined by the Grandjean–Cano technique.[23] The sign of the cholesteric phases was determined using a contact method where mixing of the samples with a doped cholesteric liquid-crystal of known negative screw sense was tested.[24] The wavelengths used for photoswitching were the ideal wavelength determined for $CHCl_3$ solution.

For the LC sample doped with three weight % *tt*-(*S*)-**1** a clear cholesteric phase was observed with a pitch of + 2.12 μm, indicating a helical twisting power (β) of + 15.2 μm^{-1}.[25] The positive screw sense of the cholesteric packing induced by an (*S*)-binaphthalene based dopant is in accordance with comparable compounds.[14] Irradiation with 396 nm increased the cholesteric pitch to +2.24 μm while subsequent irradiation with 450 nm decreased the pitch to +2.18 μm. The ratio of the three isomers *tt*-(*S*)-**1**, *ct*-(*S*)-**1** and *cc*-(*S*)-**1** in the photostationary states in the liquid-crystalline phase were determined by HPLC (Table 3).

Table 3. Photostationary state ratios of the three isomers of (*S*)-**1** doped in mesogenic host E7 (3 wt %).[a]

λ [nm^{-1}]	*tt*-(*S*)-**1** [%]	*ct*-(*S*)-**1** [%]	*cc*-(*S*)-**1** [%]	pitch [μm^{-1}]
–	100			+ 2.12
396	51	39	10	+ 2.24
450	82	16	2	+ 2.18

[a] As determined by HPLC analysis on silica gel using a gradient from pure chloroform to chloroform/Et_2O 98:2 (0.5 mL min^{-1}) and 296 nm (which is an isosbestic point of the three form this eluent) as a detection wavelength. The elution order is: *tt*-(*S*)-**1** 20.9 min, *ct*-(*S*)-**1** 22.2 min, *cc*-(*S*)-**1** 23.3 min. Cholesteric pitches were determined by the Grandjean–Cano method.

Comparing these results in an LC phase with those of a $CHCl_3$ solution (Table 2), shows a less selective *trans* to *cis* isomerization. The *cis* to *trans* isomerization on the other hand is more selective. These minor effects can be attributed to changes in the relative absorption of the various isomers in a different environment. From the experimental photostationary ratios and the cholesteric pitches the helical twisting powers of *ct*-(*S*)-**1** and *cc*-(*S*)-**1** could be calculated to be + 17.2 μm^{-1} and +13.0 μm^{-1}. All three forms have comparable helical twisting powers and azobenzene isomerization was proven to occur in a liquid crystalline environment. The switching selectivity in a LC host is similar to the switching selectivity in chloroform solution but irradiation times are prolonged. Because of the similar helical twisting powers found for *tt*-**1**, *ct*-**1** and *cc*-**1**, however, no efficient switching of cholesteric phase chirality is possible for (*S*)-**1**. This was already anticipated because the binaphthalene core, expected to be largely responsible for chiral induction in a liquid crystal, is fixed by a methylene tether and azobenzene isomerization hardly has any effect on the chirality of the core as already observed in CD experiments in chloroform solution.

Compound (*S*)-**2**, although structurally similar to (*S*)-**1**, shows completely different behavior in a liquid crystalline matrix. Again, three weight % of pure *tt*-(*S*)-**2** in nematic E7 resulted in a clear cholesteric phase with a pitch of + 3.05 μm, indicating a relatively low helical twisting power of +10.9 μm^{-1}. Irradiation with 402 nm light inverted the cholesteric pitch to −5.52 μm while subsequent irradiation at 466 nm reverted the pitch to +21.87 μm.[26] During these photoinduced cholesteric helix inversions the Grandjean–Cano lines observed through a polarization microscope moved outwards, then disappeared and upon continued irradiation appeared again. This is a unique case of direct observation of gradual cholesteric helix inversion via a compensated nematic phase using a chiroptical molecular switch. The photostationary state ratios of the three isomers *tt*-(*S*)-**2**, *ct*-(*S*)-**2** and *cc*-(*S*)-**2** in the liquid-crystalline phase determined by HPLC, using the same method as for compound **1**, are summarized in Table 4.

Table 4. Photostationary state ratios of the three isomers of (*S*)-**2** doped in mesogenic host E7 (3 wt %).[a]

λ [nm^{-1}]	*tt*-(*S*)-**2** [%]	*ct*-(*S*)-**2** [%]	*cc*-(*S*)-**2** [%]	pitch [μm^{-1}]
–	100			+ 3.05
402	35	51	14	−5.52
466	58	37	5	+ 21.87

[a] As determined by HPLC analysis on silica gel using a gradient from pure chloroform to chloroform/ether 98:2 (0.5 mL min^{-1}) and 245 nm (which is an isosbestic point of the three form this eluent) as a detection wavelength. The elution order is: *tt*-(*S*)-**1** 20.7 min, *ct*-(*S*)-**1** 22.8 min, *cc*-(*S*)-**1** 24.2 min. Cholesteric pitches were determined by the Grandjean–Cano method.

Also thermal switching back to *tt*-(*S*)-**2** starting from the 402 nm photostationary state was investigated and after heating the sample to 50 °C (where the sample is still liquid crystalline) the mixture fully reverts to >99 % *tt*-(*S*)-**2** as confirmed by HPLC analysis. The helical twisting powers of *ct*-(*S*)-**2** and *cc*-(*S*)-**2** were calculated to be −8.4 μm^{-1} and −39.3 μm^{-1}, respectively. Compound **2** can function as an efficient molecular switch in a liquid crystalline matrix and photoswitching between three different forms can be induced by light. Due to the differences in helical twisting powers of the three forms, positive for *tt*-(*S*)-**2** and negative for *ct*-(*S*)-**2** and *cc*-(*S*)-**2**, the helicity of a cholesteric liquid crystal can efficiently be controlled. Essential here are the opposite helical twisting powers for the all-*trans* and the isomerized forms of **2**.

At this point it is difficult to provide a detailed interpretation of the very different behavior of (*S*)-**1** and (*S*)-**2**, however by comparison with model compounds (*S*)-**10** and (*S*)-**11** (Figure 3), respectively, we can make the following comments. First of all, (*S*)-**10**, the model compound for the core

of (*S*)-**1**, shows a very strong HTP ($\beta = +85\ \mu m^{-1}$) in PCB (a biphenyl-like nematic liquid crystal),[14c] whilst the HTPs of the three isomers of (*S*)-**1** range between $\beta = +13$ and $+17\ \mu m^{-1}$. This indicates that the main source of the cholesteric induction of (*S*)-**1** is still the binaphthyl core which is fixed in a *cisoid* conformation by the methylene bridge. The significant reduction of HTP going from (*S*)-**10** to (*S*)-**1** could be ascribed to a more difficult alignment of the molecules of the nematic liquid crystal around the (*S*)-**1** solute, as a result of the steric hindrance due to the azo-substituents. It is also interesting to note that the above variation of HTP could also be related to a different alignment of the *tt*, *ct*, *cc* isomers of (*S*)-**1** in the nematic solvent, owing to the different shape of these compounds. Ferrarini and Spada et al. have in fact recently demonstrated that biphenyl compounds with the same absolute configuration ((*P*), for instance) can induce a (*P*)- or (*M*)-cholesteric phase in E7, depending on their disk-like or rod-like behaviour, which is, in turn, related to the molecular shape of these derivatives.[27]

On the contrary, the HTP of (*S*)-**11**, the model compound for the core of (*S*)-**2**, in K15 (a nematic solvent structurally similar to E7) is only $+1.5\ \mu m^{-1}$.[14b] Therefore the calculated HTP values of $\beta + 10.9$, -8.4 and $-39.3\ \mu m^{-1}$ of *tt*-, *ct*- and *cc*-(*S*)-**2**, respectively, could largely be attributed to the geometry around the azobenzene moieties which changes upon photoisomerization. It is remarkable that the changes in HTP on passing from the *tt*-(*S*)-**2** to *ct*-(*S*)-**2** to *cc*-(*S*)-**2** are almost additive, indicating that the effects on the overall HTP value due to the two azobenzene isomerizations are almost independent. Although the intervention of a *cisoid–transoid* isomerization of the binaphthyl moiety cannot be ruled out, the CD spectrum of (*S*)-**2** shows only very little changes after the photochemical irradiation in solution. A positive couplet is always observable: this means that the critical value of the dihedral angle for sign inversion of the CD couplet ($\theta = 110°$) is not attained.[18] Therefore, both before and after irradiation the dihedral angle of the binaphthalene moiety of (*S*)-**2** ranges between 90 and 110°. These values can be easily accepted, considering that other 1,1′-binaphthyl compounds with these characteristics are known.[18b,c] Only in the case of 2,2′-bis(bromomethyl)-1,1′-binaphthyl a dihedral angle larger than 110° was reported.[14b]

However, it is interesting to note, as we did above, that the variation of the HTP value increases with the extent of *trans–cis* isomerization of the azobenzene moieties. This supports the major role of the azobenzene isomerization on the overall geometry of the molecule. Next to a possible *cisoid–transoid* passage of the core itself due to the different steric hindrance around the binaphthyl moiety (see above), photoinduced *cis–trans* isomerization of the azobenzene moieties in (*S*)-**2** can induce a change the overall geometry and helicity of (*S*)-**2**. The observed variations of the HTP can be explained as follows; either one or two photoinduced *trans* to *cis* isomerizations of the azobenzene moieties in (*S*)-**2** give rise to a compound with an overall helicity opposite to the helicity of the binaphthyl core resulting in a reversal of the handedness of the cholesteric phase. An alternative explanation (following again Ferrarini, Spada et al.)[27] could be that azobenzene isomerization changes the alignment of the nematic solvent around the solute resulting in a different cholesteric phase.

Conclusion

We have shown that optically active binaphthyl derivatives containing two azobenzene chromophores can be prepared by straightforward chemistry in satisfactory yields starting from enantiomerically pure BINOL. Compounds (*S*)-**1** and (*S*)-**2** show interesting photochromic properties and they can act as molecular switches in solution. While compound (*S*)-**1** in the liquid crystal host E7 shows only very small variation of the cholesteric pitch, compound (*S*)-**2** in the same liquid crystalline host is capable of reversibly inverting the cholesteric packing upon photoisomerization. The all-*trans* form of (*S*)-**2** has a positive helical twisting power whereas both forms with *cis*-azobenzene moieties induce a negative helicity. The helical twisting power of the all-*cis* form of (*S*)-**2** is remarkably large. These features were thus far only observed for switches where photoisomerization resulted in a full reversal of the chirality of the molecular structure (inherently dissymmetric chiroptical switches).

The present investigation clearly shows that the chemical coupling of the photochemical properties of the azo-group with the chirality of the BINOL skeleton constitutes a practicable approach to a new class of useful chiral molecular switches. Compound (*S*)-**2** is the first example of a chiroptical molecular switch where the switching unit and the chiral moiety are separate entities that is capable to completely reverse liquid crystalline chirality.

Experimental Section

General procedures: ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker Aspect 300 (300 MHz), Varian VXR-300 (300 MHz) or Varian Gemini-200 (200 MHz). ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Aspect 300 (75 MHz), Varian VXR-300 (75 MHz) or Varian Gemini-200 (50 MHz). Chemical shifts are denoted in δ unit (ppm) relative to $CDCl_3$. The splitting patterns are designated as follows: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet) for ^{1}H NMR. For ^{13}C NMR the carbon atoms are assigned as q (primary carbon), t (secondary carbon), d (tertiary carbon) and s (quaternary carbon). Chemical ionization MS spectra were obtained with a AEI MS-902 spectrometer. The EI-MS spectra were obtained with a Jeol JMS-600 spectrometer. HPLC analyses were performed on a Waters HPLC system equipped of a 600E solvent delivery system and a 996 photodiode array detector. CD and UV/Vis analyses were performed on a JASCO J-715 spectropolarimeter and a Hewlett–Packard HP 8453 FT Spectrophotometer. Optical rotations were measured with a JASCO DIP-370 digital polarimeter and a Perkin–Elmer 241 polarimeter. THF was freshly distilled prior its use on sodium/benzophenone and stored under nitrogen atmosphere. CH_2Cl_2 was distilled from P_2O_5 and stored over activated 4 Å molecular sieves. Pyridine was distilled over CaH_2 and stored under nitrogen on KOH. *n*-Butyllithium (Aldrich) was a 1.6 M solution in *n*-hexane. Addition of organometallics were performed using syringe/septum cap techniques under nitrogen atmosphere. Commercial reagents were used without purification. Column chromatography was carried out with silica gel Merck 60 (80–230 mesh).

Photochemical isomerizations: Photoirradiation in solution were performed by irradiation of a sample in a 1 cm quartz cuvette with an 200 W

Oriel 60100 Xe-lamp attached to an Oriel Cornerstone 260 monochromator. Photostationary states are ensured by monitoring composition changes in time by taking UV spectra at distinct intervals until no changes were observed. Ratios of the different isomers of the molecular switches were determined by HPLC by monitoring at the isosbestic point. Photoisomerizations in liquid crystalline films were performed with the same light source monitoring the phase transitions through a Olympus BX 60 polarization microscope. Ratios of the different isomers were again determined by HPLC.

Preparation and analysis of liquid crystalline samples: The pitches of the liquid crystalline phases were determined by the Grandjean–Cano technique using an Olympus BX 60 polarization microscope.[28] Grandjean–Cano textures were obtained by alignment of a cholesteric liquid crystalline material on a polyimide-covered glass surface. For this purpose a glass surface (typically 6.25 cm^2) was carefully cleaned with aqueous detergent and with organic solvent (2-propanol). This clean and dry surface was spin-coated (at approximately 3000 rpm for 1 min) with commercially available polyimide AL1051 (purchased from JSR, Belgium). These coated glass surfaces were allowed to harden at 170 °C in vacuum overnight. The surface was then linearly rubbed with a velvet cloth and the LC material doped with the appropriate amount of dopant dissolved in toluene (± 5 mg mL^{-1}) was slowly poured onto this alignment layer. After evaporation of the solvent at room temperature a suitable aligned LC film was obtained. The Grandjean–Cano texture was obtained by applying a plan-convex converging lens of known radius ($R = 25.119$, 30.287, 40.388 or 50.481 mm; Linos Components; Radiometer) onto this liquid crystalline covered surface. The sign of the cholesteric phases was determined using a contact method where mixing of the samples with a doped cholesteric liquid crystal of known negative screw sense, consisting of dopant ZLI-811, obtained from Merck in the appropriate liquid crystalline host, was tested.

Synthesis

(*S*)-6,6′-Dibromo-2,2′-methylenedioxy-1,1′-binaphthalene (4): K_2CO_3 (3.5 g, 25 mmol) was added to a solution of (*S*)-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthalene (2.66 g, 6.0 mmol) in dry DMF (30 mL) under nitrogen. The reaction mixture was stirred at 80 °C for 30 min, CH_2I_2 (0.72 mL, 9 mmol) was added and stirring continued overnight at 80 °C. After cooling to RT, the reaction mixture was diluted with Et_2O (300 mL), washed with H_2O and brine, the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (silica gel, pet. ether/Et_2O 85:15) and a successive crystallization from Et_2O/*n*-hexane affording pure (*S*)-6,6′-dibromo-2,2′-methylenedioxy-1,1′-binaphthalene as white crystals (2.13 g, 78 %). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.10$ (d, 2H), 7.88 (d, $J = 9.0$ Hz, 2H), 7.50 (d, 2H), 7.38 (dd, $J = 9.0$, 1.9 Hz, 2H), 7.30 (d, 2H), 5.69 (s, 2H); EI-MS: *m*/*z*: calcd for $C_{21}H_{12}Br_2O_2$: 456.92; found: 456 [M^+].

(*S*)-6,6′-Dibromo-2,2′-diethoxy-1,1′′-binaphthalene (5): [16] K_2CO_3 (3.0 g, 22 mmol) was added under nitrogen to a solution of (*S*)-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthalene (2.22 g, 5.0 mmol) in dry DMF (18 mL). The reaction mixture was stirred at 80 °C for 30 min, bromoethane (1.1 mL, 15 mmol) was added and stirring continued overnight at 80 °C. After cooling to RT, the reaction mixture was diluted with Et_2O (300 mL), washed with H_2O and brine, the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane 4:6) and a successive crystallization from Et_2O/*n*-hexane affording pure (*S*)-6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthalene as white crystals (2.20 g, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.01$ (d, 2H), 7.85 (d, $J = 9.0$ Hz, 2H), 7.42 (d, 2H), 7.27 (dd, $J = 9.0$, 2.0 Hz, 2H), 6.96 (d, 2H), 4.1–4.2 (m, 4H), 1.06 (t, 6H); EI-MS: *m*/*z*: calcd for $C_{24}H_{20}Br_2O_2$: 497.98; found: 500 [M^+].

Preparation of $BF(OCH_3)_2$: $B(OCH_3)_3$ (6 mL, 74 mmol) and $BF_3{\cdot}Et_2O$ (2.86 mL, 23.3 mmol) were mixed and stirred at RT for 30 min. The pure product was obtained by distillation collecting fractions between 50–52 °C. The product was immediately used for the following reactions.

(*S*)-6,6′-Dihydroxy-2,2′-methylenedioxy-1,1′-binaphthalene (6): A solution of *n*BuLi 1.6 M in *n*-hexane (3.9 mL, 6.25 mmol) under nitrogen was added at −70 °C to a solution of (*S*)-6,6′-dibromo-2,2′-methylenedioxy-1,1′-binaphthalene (**4**; 1.140 g, 2.5 mmol) in dry THF (35 mL). The solution was stirred at −70 °C for 15 min, $BF(OCH_3)_2$ (0.750 mL, 6.25 mmol) was added and the temperature was slowly increased until −10 °C. A solution of 30 % aq. H_2O_2 (2.875 mL, 25 mmol) and 0.5 M aq. NaOH (3 mL) was added and the overall reaction mixture was stirred while reaching RT. The reaction mixture was diluted with Et_2O (200 mL), washed with brine and the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (silica gel, Et_2O/*n*-hexane 8:2) affording pure (*S*)-6,6′-dihydroxy-2,2′-methylenedioxy-1,1′-binaphthalene (**6**) as a white solid (710 mg, 86 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.74$ (d, $J = 8.8$ Hz, 2H), 7.37 (d, $J = 8.8$ Hz, 2H), 7.36 (d, $J = 9.2$ Hz, 2H), 7.18 (d, $J = 2.5$ Hz, 2H), 6.86 (dd, $J = 9.2$, 2.5 Hz, 2H), 5.60 (s, 2H), 4.9 (s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 100.5$ (t), 107.5 (d), 115.4 (d), 119.0 (d), 123.7 (s), 124.8 (s), 126.1 (d), 126.2 (d), 130.5 (s), 146.9 (s), 150.2 (s); CI-MS: *m*/*z*: calcd for $C_{12}H_{14}O_4$: 330.09; found: 348 [$M+NH_4^+$].

(*S*)-6,6′-Dihydroxy-2,2′-diethoxy-1,1′-binaphthalene (7): A solution of *n*BuLi 1.6 M in *n*-hexane (3.9 mL, 6.25 mmol) was added under nitrogen at −70 °C to a solution of (*S*)-6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthalene (**5**; 1.250 g, 2.5 mmol) in dry THF (35 mL). The solution was stirred at −70 °C for 15 min, $BF(OCH_3)_2$ (0.750 mL, 6.25 mmol) was added and the temperature was slowly increased to −10 °C. A solution of 30 % aq. H_2O_2 (2.875 mL, 25 mmol) and 0.5 M aq. NaOH (3 mL) was added and the overall mixture was stirred while reaching RT. The reaction mixture was diluted with Et_2O (200 mL), washed with brine and the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (silica gel, Et_2O/*n*-hexane, 8:2) affording pure (*S*)-6,6′-dihydroxy-2,2′-diethoxy-1,1′-binaphthalene (**7**) as a white solid (670 mg, 72 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.74$ (d, $J = 8.9$ Hz, 2H), 7.38 (d, $J = 8.9$ Hz, 2H), 7.12 (d, $J = 2.5$ Hz, 2H), 7.03 (d, $J = 9.1$ Hz, 2H), 6.81 (dd, $J = 9.1$, 2.5 Hz, 2H), 4.91 (s, 2H), 4.0 (q, $J = 7.0$ Hz, 4H), 1.05 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 12.6$ (q), 63.2 (t), 106.9 (d), 114.6 (d), 115.6 (d), 118.7 (s), 124.9 (2d), 126.9 (s), 127.8 (s), 149.2 (s), 150.1 (s); CI-MS: *m*/*z*: calcd for $C_{24}H_{22}O_4$: 374.15; found: 392 [$M+NH_4^+$].

(*S*)-6,6′-Dihydroxy-5,5′-bisbenzeneazo-2,2′-methylenedioxy-1,1′-binaphthalene (8): Dry pyridine (0.4 mL, 5 mmol) and K_2CO_3 (690 mg, 5 mmol) was added at −10 °C to a solution of (*S*)-6,6′-dihydroxy-2,2′-methylenedioxy-1,1′-binaphthalene (**6**; 363 mg, 1.1 mmol) in dry THF (20 mL) under a nitrogen atmosphere. The solution was stirred at −10 °C for 5 min, dry benzenediazonium tetrafluoborate (634 mg, 3.3 mmol) was added and the reaction mixture was stirred for 40 h at −10 °C. The red solution was diluted with Et_2O (200 mL), washed with NH_4Cl, H_2O and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by two successive column chromatography (silica gel; toluene/Et_2O 96:4, then silica gel, CH_2Cl_2) affording pure (*S*)-6,6′-dihydroxy-5,5′-bisbenzeneazo-2,2′-methylenedioxy-1,1′-binaphthalene (**8**) as a red solid (225 mg, 38 %). $[\alpha]_D^{25} = -150$ ($c = 1.0$ in chloroform). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 16.23$ (s, 2H), 8.79 (d, $J = 9.5$ Hz, 2H), 7.81 (d, $J = 7.3$ Hz, 4H), 7.45–7.6 (m, 8H), 7.36 (t, $J = 7.3$ Hz, 2H), 6.82 (dd, $J = 9.8$, 2.2 Hz, 2H), 5.68 (s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 100.5$ (t), 116.5 (d), 116.6 (d), 120.1 (d), 121.4 (d), 122.6 (d), 124.4 (s), 124.8 (s), 125.5 (d), 127.1 (d), 127.5 (s), 129.3 (s), 134.4 (d), 142.8 (s), 148.7 (s), 166.5 (s); CI-MS: *m*/*z*: calcd for $C_{33}H_{22}N_4O_4$: 538.16; found: 539 [$M+H^+$].

(*S*)-6,6′-Dihydroxy-5,5′-bisbenzeneazo-2,2′-diethoxy-1,1′-binaphthalene (9): Dry pyridine (about 0.2 mL, 3 mmol) and K_2CO_3 (414 mg, 3 mmol) was added at −10 °C to a solution of (*S*)-6,6′-dihydroxy-2,2′-diethoxy-1,1′-binaphthalene (**7**; 224 mg, 0.6 mmol) in dry THF (10 mL) under a nitrogen atmosphere. The solution was stirred at −10 °C for 5 min, dry benzenediazonium tetrafluoborate (345 mg, 1.8 mmol) was added and the reaction mixture was stirred for 40 h at −10 °C. The red solution was diluted with Et_2O (150 mL), washed with NH_4Cl, H_2O and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by two successive column chromatography separations (silica gel, toluene/CH_2Cl_2/Et_2O 70:27:3 then silica gel, *n*-hexane/Et_2O 6:4) affording pure (*S*)-6,6′-dihydroxy-5,5′-bisbenzeneazo-2,2′-diethoxy-1,1′-binaphthalene (**9**) as a dark red solid (149 mg, 43 %). $[\alpha]_D^{25} = -28$ ($c = 1.0$ in chloroform). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 16.15$ (s, 2H), 8.64 (d, $J = 9.0$ Hz, 2H), 7.48 (t, $J = 7.3$ Hz, 4H), 7.35 (d, $J = 9.0$ Hz, 4H), 7.28 (t, $J = 7.3$ Hz, 2H), 7.20 (d, $J = 9.8$ Hz, 2H), 6.66 (d, $J = 9.8$ Hz, 2H), 4.06 (q, $J = 6.9$ Hz, 4H), 1.14 (t, $J = 6.9$ Hz, 6H); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 13.3$ (q), 63.3 (t), 114.1 (d), 116.6 (d), 120.8 (s),

121.5 (d), 124.1 (d), 125.3 (d), 126.2 (s), 127.1 (s), 128.1 (d), 128.9 (s), 136.8 (d), 143.1 (s), 153.4 (s), 171.2 (s); CI-MS: *m*/*z*: calcd for $C_{36}H_{30}N_4O_4$: 582.23; found: 583 [*M*+H$^+$].

(*S*)-6,6′-Dimethoxy-5,5′-bisbenzeneazo-2,2′-methylenedioxy-1,1′-binaphthalene (1): K_2CO_3 (138 mg, 1.0 mmol) was added under nitrogen at RT to a solution of (*S*)-6,6′-dihydroxy-5,5′-bisbenzeneazo-2,2′-methylenedioxy-1,1′-binaphthalene (**8**; 108 mg, 0.20 mmol) in dry DMF (2 mL). The solution was stirred at 60 °C for 30 min, MeI (38 μL, 0.60 mmol) was added and the reaction mixture was stirred overnight at 60 °C. After cooling to RT, the reaction mixture was diluted with Et_2O (50 mL), washed with H_2O and brine, the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. All the successive operations were performed keeping the product away from light. The residue was dissolved in toluene, stirred at 80 °C for 1 h and concentrated in vacuo. The product was purified by two successive column chromatography separations (silica gel, CH_2Cl_2/pet. ether 85:15 then silica gel, *n*-hexane/Et_2O 1:1) affording pure (*S*)-6,6′-dimethoxy-5,5′-bisbenzeneazo-2,2′-methylenedioxy-1,1′-binaphthalene (**1**) as a dark orange solid (73 mg, 65 %). $[\alpha]_D^{25} = -78$ (c = 0.05 in chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46 (d, J = 9.0 Hz, 2H), 8.09 (m, 4H), 7.55–7.65 (m, 6H), 7.52 (d, J = 9.0 Hz, 2H), 7.24 (d, J = 9.0 Hz, 2H), 5.71 (s, 2H), 3.98 (s, 6H); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 55.9 (q), 101.6 (t), 113.6 (d), 121.0 (d), 121.3 (d), 124.0 (d), 124.3 (s), 125.7 (s), 126.4 (s), 127.7 (d), 127.9 (d), 129.7 (d), 135.4 (s), 145.6 (s), 148.8 (s), 151.9 (s); CI-MS: *m*/*z*: calcd for $C_{35}H_{26}N_4O_4$: 566.20; found: 567 [*M*+H$^+$].

(*S*)-6,6′-Dimethoxy-5,5′-bisbenzeneazo-2,2′-diethoxy-1,1′-binaphthalene (2): K_2CO_3 (104 mg, 0.75 mmol) was added at RT under nitrogen to a solution of (*S*)-6,6′-dihydroxy-5,5′-bisbenzeneazo-2,2′-diethoxy-1,1′-binaphthalene (**9**; 87 mg, 0.15 mmol) in dry DMF (1.5 mL). The solution was stirred at 60 °C for 30 min, MeI (28 μL, 0.45 mmol) was added and the reaction mixture was stirred overnight at 60 °C. After cooling to RT, the reaction mixture was diluted with Et_2O (40 mL), washed with H_2O and brine, the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. All the successive operations were performed keeping the product away from light. The residue was dissolved in toluene, stirred at 80 °C for 1 h and concentrated in vacuo. The product was purified by two successive column chromatography separations (silica gel, CH_2Cl_2/pet. ether 85:15 then silica gel, *n*-hexane/Et_2O 1:1) affording pure (*S*)-6,6′-dimethoxy-5,5′-bisbenzeneazo-2,2′-diethoxy-1,1′-binaphthalene (**2**) as a dark orange solid (60 mg, 66 %). $[\alpha]_D^{25} = -445$ (c = 0.05 in chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.47 (d, J = 9.4 Hz, 2H), 8.05 (m, 4H), 7.5–7.65 (m, 6H), 7.45 (d, J = 9.4 Hz, 2H), 7.15–7.25 (m, 4H), 4.02 (q, J = 6.9 Hz, 4H), 1.08 (t, J = 6.9 Hz, 6H); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 13.6 (q), 56.0 (q), 63.8 (t), 113.9 (d), 116.1 (d), 119.0 (s), 121.2 (d), 122.6 (s), 123.0 (d), 127.2 (d), 127.7 (d), 128.6 (s), 129.4 (d), 135.1 (s), 145.4 (s), 151.9 (s), 152.1 (s); CI-MS: *m*/*z*: calcd for $C_{38}H_{34}N_4O_4$: 610.26; found: 611 [*M*+H$^+$].

Acknowledgments

C.R. and T.M. thank the Università della Basilicata, and MIUR-COFIN 2001 (New theoretical and experimental methods for the assignment of the molecular absolute configuration in solution") for financial support. Financial support from the National Research School Catalysis (NRSC-C) to B.L.F. and R.A.v.D. and The Netherlands Foundation for Scientific Research (NWO-CW) are gratefully acknowledged.

[1] a) *Sci. Amer.* Special Issue: *Nanotech: The Science of Small Gets Down to Business*, September **2001**; b) R. P. Feynman in *Miniaturization* (Ed.: H. D. Gilbert), New York, **1971**; c) K. E. Drexler, *Nanosystems: Molecular Machinery, Manufacturing and Computation*, Wiley, New York, **1992**; d) R. D. Astumian, *Sci. Amer.* **2001**, *285*, 56–64.

[2] *Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCH, Weinheim, **2001**.

[3] Special Issue: Photochromism: Memories and Switches, *Chem. Rev.* **2000** (Guest Ed.: M. Irie), *100*, 1683–1890.

[4] See for example: a) O. Pieroni, A. Fissi, G. Popova, *Prog. Polym. Sci.* **1998**, *23*, 81–123; b) F. Ciardelli, O. Pieroni, A. Fissi, C. Carlini, A. Altomare, *Br. Polym. J.* **1989**, *21*, 97–106; c) M. Irie, *Adv. Polym. Sci.* **1990**, *94*, 27–67; d) *Applied Photochromic Polymer Systems* (Ed.: C. B. McArdle), Blackie, Glasgow (UK), **1992**; e) F. Ciardelli, O. Pieroni, A. Fissi, *J.* L. Houben, *Biopolymers* **1984**, *23*, 1423–1437; f) O. Pieroni, F. Ciardelli, *Trends Polym. Sci.* **1995**, *3*, 282–287; g) T. Kinoshita, *Prog. Polym. Sci.* **1995**, *20*, 527–583; h) I. Willner, *Acc. Chem. Res.* **1997**, *30*, 347–356.

[5] F. Ciardelli, O. Pieroni in *Chiroptical Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCH, Weinheim, **2001**, Chapter 13, pp. 399–441.

[6] M. Irie, S. Kobatake, M. Horichi, *Science* **2001**, *291*, 1769–1772.

[7] T. Ikeda, A. Kanazawa in *Chiroptical Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCH, Weinheim, **2001**, Chapter 12, pp. 363–397.

[8] a) B. L. Feringa, R. A. van Delden, N. Koumura, E. M. Geertsema, *Chem. Rev.* **2000**, *100*, 1789–1816; b) B. L. Feringa, R. A. van Delden, M. K. J. ter Wiel in *Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCH, Weinheim, **2001**, Chapter 5, pp. 123–163.

[9] B. L. Feringa, N. P. M. Huck, H. A. van Doren, *J. Am. Chem. Soc.* **1995**, *117*, 9929–9930.

[10] See for example: a) T. Yamaguchi, K. Uchida, M. Irie, *J. Am. Chem. Soc.* **1997**, *119*, 6066–6071; b) T. Yamaguchi, Y. Tanaka, H. Nakazumi, K. Uchida, T. Yamada, M. Irie, *Enantiomer* **2001**, *6*, 309–311; c) Y. Yokoyama, S. Uchida, Y. Shimizu, Y. Yokoyama, *Mol. Cryst. Liq. Cryst.* **1997**, *297*, 85–91; d) Y. Yokoyama, S. Uchida, Y. Yokoyama, Y. Sugawara, Y. Kurita, *J. Am. Chem. Soc.* **1996**, *118*, 3100–3107; e) L. Eggers, V. Buß, *Angew. Chem.* **1997**, *109*, 885–887; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 881–883; f) A. Miyashita, A. Iwamoto, T. Kuwayama, H. Shitara, Y. Aoki, M. Hirano, H. Nohira, *Chem. Lett.* **1997**, 965–966; g) T. Ikeda, T. Sasaki, K. Ichimura, *Nature* **1993**, *361*, 428; h) T. Kusumoto, K. Sato, K. Ogino, T. Hiyama, S. Takehara, M. Osawa, K. Nakamura, *Liq. Cryst.* **1993**, *14*, 727–732; i) M. Negishi, O. Tutsumi, T. Ikeda, T. Hiyama, *J.* Kawamura, M. Aizawa, S. Takehara, *Chem. Lett.* **1996**, 319–320; j) M. Negishi, K. Kanie, T. Ikeda, T. Hiyama, *Chem. Lett.* **1996**, 583–584; k) T. Ikeda, O. Tsutsum, *Science* **1995**, *268*, 1873–1875.

[11] See for example: a) S. Z. Janicki, G. B. Schuster, *J. Am. Chem. Soc.* **1995**, *117*, 8524–8527; b) Y. Yokoyama, T. Sagisaka, *Chem. Lett.* **1997**, 687–688; c) C. Denekamp, B. L. Feringa, *Adv. Mater.* **1998**, *10*, 1080–1082; d) C. Ruslim, K. Ichimura, *Adv. Mater.* **2001**, *13*, 37–40; e) G. Heppke, H. Marshall, P. Nurnberg, F. Oestreicher, G. Sherowsky, *Chem. Ber.* **1981**, *114*, 2501–2518.

[12] S. Pieraccini, S. Masiero, G. P. Spada, G. Gottarelli, *Chem. Commun.* **2003**, 598–599.

[13] a) C. Rosini, L. Franzini, A. Raffaelli, P. Salvadori, *Synthesis* **1992**, 503–517; b) L. Pu, H.-B. Yu, *Chem. Rev.* **2001**, *101*, 757–824; c) B. L. Feringa, *Acc. Chem. Res.* **2000**, *33*, 346–353.

[14] a) G. Gottarelli, M. Hibert, B. Samori, G. Solladié, G. P. Spada, R. Zimmermann, *J. Am. Chem. Soc.* **1983**, *105*, 7318–7321; b) G. Gottarelli, G. P. Spada, R. Bartsch, G. Solladié, R. Zimmermann, *J. Org. Chem.* **1986**, *51*, 589–592; c) G. Solladié, G. Gottarelli, *Tetrahedron* **1987**, *43*, 1425–1437; d) P. V. Shibaev, K. Schaumberg, T. Bjornholm, *Mol. Cryst. Liq. Cryst.* **2000**, *338*, 181–195; e) G. Gottarelli, G. P. Spada, *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 377; f) P. V. Shibaev, R. Vinokur, H.-J. Deussen, T. Bjørnholm, K. Schaumberg, *SPIE* **1997**, *3319*, 185 .

[15] a) A. Ferrarini, G. J. Moro, P. L. Nordio, *Liq. Cryst.* **1995**, *189*, 397–399; b) A. Ferrarini, G. J. Moro, P. L. Nordio, *Phys. Rev. E* **1996**, *53*, 681–688.

[16] G. D. Y. Sogah, D. J. Cram, *J. Am. Chem. Soc.* **1979**, *101*, 3035–3042.

[17] H. J. Deussen, E. Hendrickx, C. Boutton, D. Krog, K. Clays, K. Bechgaard, A. Persoons, T. Bjornholm, *J. Am. Chem. Soc.* **1996**, *118*, 6841–6852.

[18] a) S. F. Mason, R. H. Seal, D. R. Roberts, *Tetrahedron* **1974**, *30*, 1671–1682; b) C. Rosini, I. Rosati, G. P. Spada, *Chirality* **1995**, *7*, 353–358; c) C. Rosini, S. Superchi, H. W. I. Peerlings, E. W. Meijer, *Eur. J. Org. Chem.* **2000**, 61–71.

[19] H. Suzuki, *Electronic Absorption Spectra and Geometry of Organic Molecules*, Academic Press, New York, **1967**, p. 503.

[20] J. J. G. S. van Es, H. A. M. Biemans, E. W. Meijer, *Tetrahedron: Asymmetry* **1997**, *8*, 1825–1831.

[21] H. Rau in *Photochromism, molecules and systems* (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam, **1990**, Chapter 4, pp. 165–192.
[22] a) Z. Sekkat, W. Knoll *J. Opt. Soc Am. B* **1995**, *12*, 1855–1867; b) O. Watanabe, M. Tsuchimori, A. Okada, *J. Mater. Chem.* **1996**, *6*, 1487–1492; c) C. Egami, Y. Suzuki, O. Sugihara, N. Okamoto, H. Fujimura, K. Nakagawa, H. Fujiwara, *Appl. Phys. B* **1997**, *64*, 471–478; d) C. Wang, H. Fei. , Y. Yang, Z. Wei, Y. Qui, Y. Chen, *Opt. Commun.* **1999**, *159*, 58–62.
[23] a) G. Heppke, F. Oesterreicher, *Z. Naturforsch. A* **1977**, *32*, 899–901; b) G. Gottarelli, B. Samori, C. Stremmenos, G. Torre, *Tetrahedron* **1981**, *37*, 395–399.
[24] G. Solladié, R. G. Zimmermann, *Angew. Chem.* **1984**, *96*, 335–349; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 348–362.
[25] Helical twisting power: $\beta=(pcr)$-1, where p is the pitch (μm), c is the concentration (g of dopant per gram of LC solution) and r is the enantiomeric purity of the dopant.
[26] Light of 402 nm proved to be a slightly more selective wavelength for switching in an LC phase, in solution the selectivity observed upon irradiation with this wavelength is slightly (about 2%) less than the ideal 405 nm.
[27] A. di Matteo, S. M. Todd, G. Gottarelli, G. Solladié, V. E. Williams, R. P. Lemieux, A. Ferrarini and G. P. Spada, *J. Am. Chem. Soc.* **2001**, *123*, 7842–7851.
[28] a) F. Grandjean, *C. R. Acad. Sci.* **1921**, *172*, 71; b) R. Cano, *Bull. Soc. Fr. Mineral* **1968**, *91*, 20.

Received: June 26, 2003 [F5276]